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Sol-Gel Synthesis of MgO-SiO_2 Glass Compositions Having Stable Liquid-Liquid Immiscibility

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Narottam P. Bansal
Lewis Research Center
Cleveland, Ohio

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April 1987

Figure 17: Label should read: H_2O:TEOS mole fraction = 7.5

Summary and Abstract: Last sentence should read

"The overall activation energy for gel formation in $10MgO$-$90SiO_2$ (mol %) system for water:TEOS mole ratio of 7.5 was calculated to be 58.7 kJ/mol."

SOL-GEL SYNTHESIS OF MgO-SiO_2 GLASS COMPOSITIONS HAVING STABLE LIQUID-LIQUID IMMISCIBILITY

Narottam P. Bansal
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-3599

SUMMARY

MgO-SiO_2 glasses containing upto 15 mol % MgO, which could not have been prepared by the conventional glass melting method due to the presence of stable liquid-liquid immiscibility, have been synthesized by the sol-gel technique. Clear and transparent gels were obtained from the hydrolysis and polycondensation of silicon tetraethoxide (TEOS) and magnesium nitrate hexahydrate when the water: TEOS mole ratio was four or more The gelling time decreased with increase in magnesium content, water: TEOS ratio, and reaction temperature. Magnesium nitrate hexahydrate crystallized out of the gels containing 15 and 20 mol % MgO on slow drying. This problem was partially alleviated by drying the gels quickly at higher temperatures. Monolithic gel samples were prepared using glycerol as the drying control chemical additive. The gels were subjected to various thermal treatments and characterized using techniques such as DTA, TGA, IR-spectroscopy, x-ray diffraction, surface area and pore size distribution measurements. No organic groups could be detected in the glasses after heat treatments to ~800 °C, but trace amounts of hydroxyl groups were still present. No crystalline phase was found from x-ray diffraction in the gel samples heated to ~890 °C. At higher temperatures, alpha quartz precipitated out as the crystalline phase in gels containing up to 10 mol % MgO. The weak diffraction peaks in heated samples containing 15 and 20 mol % MgO could not be assigned to any known phase. The overall activation energy for gel formation in $10MgO$-$90SiO_2$ (mol %) system for water: TEOS mole ratio of 7.5 was calculated to be 58.7 kJ/mol.

INTRODUCTION

Glass compositions within the stable liquid-liquid immiscibility region cannot be prepared by the conventional glass melting method. However, such glass compositions may be obtained by the sol-gel technique using metal alkoxides and metal salts as the starting materials. The free energy of a gel is higher (ref. 1) than that of the glass of the same composition. It should, therefore, be possible to convert a gel into glass at temperatures much below the liquidus temperature. The gelling process is influenced by various parameters such as temperature, pH, chemical nature of the alkoxides and other reactants, water to alkoxide ratio, presence of a catalyst, concentration of the reactants, and the nature of the solvent. The sol-gel method has several advantages such as better homogeneity as mixing takes place at the molecular level, higher purity, lower processing temperatures, and most significantly the possibility of producing glasses of new compositions. The scientific and technological significance of forming glasses below their melting, phase separation, or crystallization temperature is obvious. Potential to form new materials which are structurally unstable at high temperatures also exists. The

sol-gel technique has attracted the attention of many researchers (refs. 2 to 10) and has become quite popular during the past few years. It has been used for the preparation of glasses, fibers, protective and other coatings, optical films, ultrapure monosized fine ceramic powders, composite materials, etc. Oxide glasses, including those of $CaO-SiO_2$, $SrO-SiO_2$, ZrO_2-SiO_2 systems, which are difficult to make by melting have been synthesized (refs. 11 to 15) by the sol-gel procedure.

The present study was undertaken with the primary objective of synthesizing $MgO-SiO_2$ glasses containing various mol % of MgO lying within the stable liquid-liquid immiscibility composition range by the sol-gel technique. Such glasses cannot be prepared by the conventional glass melting methods. Another purpose of this work was to prepare compositionally homogeneous precursor materials for use in studies of the effects of microgravity on phase separation in glasses. Gels of different compositions in the binary $MgO-SiO_2$ system were synthesized under various experimental conditions, subjected to different thermal treatments, and characterized using a number of techniques. The results of these investigations are reported in this paper.

EXPERIMENTAL METHODS

Gel Synthesis

Tetraethoxy silane (TEOS), $Si(OC_2H_5)_4$, and magnesium acetate tetrahydrate from Alfa Products, magnesium nitrate hexahydrate, $Mg(NO_3)_2.6H_2O$, of analytical reagent grade from Mallinckrodt and 200 proof absolute ethyl alcohol were used without further treatment. Magnesium ethoxide is easily available but has only limited solubility in alcohol. Therefore, the method of McCarthy and Roy (ref. 16) was employed to incorporate magnesium oxide into the gel. Magnesium nitrate hexahydrate was chosen as the source of magnesium oxide due to its good solubility in alcohol as well as in water. A similar approach has also been adopted by other workers (refs. 11 to 14 and 17 and 18) to introduce other metal oxides into the gels such as CaO, SrO, Na_2O, La_2O_3, Al_2O_3, in the form of their soluble metal salts. The chemical compositions of the glasses along with their acronyms are shown in table I. Figure 1 is a partial phase diagram of the $MgO-SiO_2$ system showing the compositions of this study fall in the liquid-liquid immiscibility dome. An outline of the procedure used for glass synthesis by the sol-gel process is shown in figure 2. Magnesium nitrate hexahydrate was dissolved in alcohol and mixed under stirring with TEOS which had been diluted with alcohol. The quantities of various chemicals used are listed in table II. Alcohol acts as the mutual solvent for TEOS and water which are immiscible with each other. The necessary amount of water was then added dropwise under vigorous stirring. A clear homogeneous solution resulted. The beaker containing the solution was covered and allowed to stand for gelling under ambient conditions or in a constant temperature bath. It took several hours to many days for gelation of the solutions depending upon the H_2O:TEOS mole ratio, magnesium concentration, and the reaction temperature. Monolithic, clear, and transparent bulk gels were formed which slowly cracked into smaller pieces on slow drying at room temperature. The gels were dried for several days under ambient conditions followed by heat treatments at various temperatures. Gels containing 15 and 20 mol % MgO had a tendency to crystallize on slow drying at room temperature and slowly converted into a white powder on storage. In these gels surface crystallization was evident visually and from x-ray diffraction (fig. 3) these crystals were identified to be of

$Mg(NO_3)_2.6H_2O$. To alleviate this problem another batch of gel was dried at 76 °C. No crystallization was visibly evident in these dried gels but powder x-ray diffraction again showed the presence of magnesium nitrate hexahydrate crystals in gel containing 20 mol % MgO. Gels were transformed into colorless, transparent amorphous solids by subjecting them to different heat treatments under isothermal and athermal conditions. Attempts to prepare gels using magnesium acetate tetrahydrate as the source of MgO were not successful and resulted only in nonhomogeneous white powders.

Monolithic gel bodies of 10MS composition were prepared using glycerol as the drying control chemical additive. Tremendous shrinkage took place on drying slowly under ambient conditions. On drying, the gel volume had reduced to about one-tenth of its original volume. No cracks were present in the dried cylindrical gel bodies as shown in figure 4.

Characterization of Gels

Chemical and structural evolution of gels after various thermal treatments was followed by several techniques. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using Perkin-Elmer DTA-1700 and TGS-2 systems, respectively, which were interfaced with a computerized data acquisition and analysis system. A Netzsch thermal analyzer STA-429 with a super kanthal heating element furnace was also used for simultaneous recording of DTA and TGA on the same sample. Infrared transmission spectra were recorded from 400 to 4000 cm^{-1} using the KBr pellet method with a Perkin-Elmer 1750 Infrared Fourier Transform Spectrometer interfaced with a Perkin-Elmer 7300 professional computer. Powder x-ray diffraction measurements were made at room temperature with a Phillips ADP-3600 automated powder diffractometer equipped with a crystal monochromator, employing $CuK\alpha$ radiation in the 2θ range 10 to 90°. BET surface area and pore volume measurements were made from the nitrogen adsorption isotherms at 77 K using Micromeritics Digisorb 2500 pore analysis system. Krypton gas adsorption was used for some samples of low surface area.

RESULTS

Gel Formation

Time of gelation and physical appearance of $MgO-SiO_2$ gels of various compositions for H_2O:TEOS mole ratio of ~5 are given in table II. All the gels were clear and transparent. There was not much change in solution pH on gelation. For example, the pH values of 15 and 20MS solutions immediately after the addition of water were 4.34 and 4.22 and gradually decreased to 3.90 and 3.85, respectively, just before gelation was complete. In contrast, Yamane and Kojima (ref. 13) observed an increase in pH during hydrolysis of alcoholic solutions of silicon tetramethoxide and strontium nitrate. The variation in gelling time as a function of magnesium oxide content is shown in figure 5. Gelling time is seen to decrease with increase in magnesia concentration. Experimental data showing the effect of reaction temperature on time of gel formation for $10MgO-90SiO_2$ (mol %) composition for H_2O:TEOS mole ratio of 7.5 are given in table III. Gelling time sharply decreases with rise in reaction temperature. At all temperatures the resulting gels were transparent and clear. Influence of starting materials and H_2O:TEOS ratio on gelling time and appearance of gels of $10MgO-90SiO_2$ (mol %) composition are is presented in table IV.

Effect of H_2O:TEOS ratio on time of gelation is depicted in figure 6. The gelling time is seen to decrease sharply with increase in H_2O:TEOS ratio. Clear and transparent gels were obtained only for systems using alcoholic magnesium nitrate and TEOS and H_2O:TEOS mole ratios of 4 or more. Use of an alcoholic solution of magnesium acetate as the source of magnesium oxide resulted only in a white powder, probably by the crystallization of magnesium acetate tetrahydrate. In systems with H_2O:TEOS ratios of 0.67 and 2.68, nonhomogeneous bulk gels with white crystals on the gel surface, probably of magnesium nitrate hexahydrate, were formed.

Pyrolysis of Gels

All gels were clear and transparent after drying at ~76 °C for a few days in air. The x-ray spectra showed weak diffraction peaks of magnesium nitrate hexahydrate phase in gel containing 20 mol % magnesium oxide. The dried gels of different compositions were heated to 800 °C (15MS to 780 °C and 20MS to 740 °C) in flowing air at ~3 °C/min and furnace cooled. All of these fired samples were clear, transparent and amorphous to x-rays. These amorphous samples were further subjected to various thermal treatments. One part was isothermally sintered in air at ~895 °C for 7.5 hr. After this heat treatment all compositions remained amorphous to x-rays except that some weak diffraction peaks of alpha quartz (ref. 19) were present in 2MS only. The 15MS and 20MS samples had turned white and opaque whereas 5MS, 10MS, and M9S were partly opaque and partly transparent. The 2MS composition appeared mostly glassy and transparent along with a few white opaque pieces. Another part was heated at 1000 °C for 2 hr. All samples had turned opaque white. X-ray diffraction peaks of alpha quartz (ref. 19) were found in 2MS, 5MS, 10MS, and M9S along with an amorphous halo in 10MS and M9S. The peak intensities in M9S were much higher than in 10MS which was mostly amorphous. The 15MS and 20MS were found to be amorphous except for a small peak at d = 3.754 Å (2θ = 23.7°) of an unknown phase. Powder x-ray diffraction of 2MS and 5MS compositions which had been further fired at 1100 °C for 2 hr and at 1200 °C for 1 hr showed the presence of sharp peaks of alpha quartz (ref. 19) only.

In another experiment, the 10MS composition was subjected to several isothermal heat treatments at different temperatures for various lengths of time in air. A clear transparent gel with a very light yellowish tinge was obtained on drying at 72 °C for more than six days. The light yellowish color persisted even after firing at 300 °C for 20 hr. On further heating at 500 °C for 23 hr, the sample became colorless, glassy transparent and remained so even after firing at 700 °C for 22.5 hr and at 795 °C for 8.5 hr. When the sample was further heated at 890 °C for 7.5 hr, some pieces were still transparent and colorless whereas some pieces had turned opaque white. It became fully white and opaque after sintering for 2 hr at 1000 °C.

Thermal Analysis

Thermoanalyses were performed on the as-dried gels. Typical differential thermal analysis (DTA) and thermogravimetric (TGA) curves for a room temperature dried gel of 10MS composition are shown in figure 7. DTA thermograms of gels of various compositions are presented in figure 8. The broad endothermic peak in the DTA curve is attributed to the evaporation of residual water and alcohol entrapped in micropores of the gel and decomposition of nitrate. The

TGA curve shows a substantial weight loss in the temperature region corresponding to the endothermic DTA peak, indicating that a large portion of water and organic materials are being removed and that the metal nitrate decomposes below ~400 °C. A DTA exothermic peak ascribed to oxidation of the organic impurities is occasionally observed at higher temperature but was not seen in this work. It may also be noted that a gradual and slight weight loss is continued at higher temperatures in the TGA. This is probably due to condensation dehydration of hydroxyl groups. The exothermic peak at ~900 °C in the DTA could be assigned to crystallization of glass. Another exothermic peak at higher temperature in DTA of 2MS and 5MS may be due to some polymorphic phase transformation or crystallization of another phase. Investigation of this phase was not pursued any further.

Infrared Spectroscopy

Infrared absorption spectra in the 400 to 4000 cm^{-1} range for the 10MS composition gel dried at 72 °C for more than six days is given in figure 9. The effect of various thermal treatments on the infrared absorption of 10MS is presented in figure 10. Figure 11 shows the infrared spectra of gels of various compositions after having been fired to higher temperatures at ~3 °C/min in flowing air and furnace cooled. Various absorption peaks observed in the infrared spectra of gels and glasses of the $MgO-SiO_2$ system and their assignments (refs. 20 to 28) are listed in table V. The peak due to Si-OH bonds containing nonbridging oxygen is located at 958 cm^{-1}. As the temperature of heat treatment is increased the absorption peak due to Si-OH bonds becomes weak and finally disappears at 500 °C, indicating that residual Si-OH bonds polymerize above this temperature. The strongest absorption peak is observed at ~1078 cm^{-1} which is ascribed to Si-O-Si stretching vibration. Varshneya and Suh (ref. 29), and Kamiya et al. (ref. 21) reported a slight shift of this band (1080 cm^{-1}) to higher wavenumbers with increase in heating temperature due to strengthening of the Si-O bonds in the SiO_4 tetrahedron. However, no such shift is observed in the present work. Other peaks related to Si-O bonds are those around 800 and 460 cm^{-1} attributed to bending modes of O-Si-O and Si-O-Si bonds, respectively. The intensity of the peak around 1385 cm^{-1} assigned (ref. 27) to $-NO_3$ group increased with increasing content of magnesium nitrate in the gel. The $-NO_3$ peak intensity decreased with increase in temperature of heat treatment and completely disappeared at ~500 °C. A very weak nitrate absorption band in the 300 °C fired sample implies slow decomposition of nitrate at this temperature. The bands around 3450 and 1645 cm^{-1} are assigned to absorptions due to water. The intensities of these peaks become weaker with increase in firing temperature. Specimens fired at 890 °C still contained traces of water but no absorption peaks attributable to organic groups were present.

X-ray Diffraction

The structural evolution of the gels as a function of heat treatment was followed by powder x-ray diffraction. Figure 12 shows x-ray diffraction spectra of gels of various compositions dried at ~76 °C. After drying for more than six days at ~76 °C, gels of 2MS, 5MS, 10MS, and 15MS compositions were amorphous to x-rays whereas x-ray diffraction patterns of the 20MS gel showed partial crystallization of magnesium nitrate hexahydrate along with an amorphous halo. On heating slowly to 800 °C (780 °C for 15MS and 740 °C for 20MS) in flowing air at ~3 °C/min, all gels converted into clear and transparent

solids which were amorphous to x-rays as shown in figure 13. X-ray diffraction spectra of 10MS gel fired at different temperatures for various lengths of time are presented in figure 14 which shows its amorphous nature even at 899 °C. After firing for 7.5 hr at 899 °C in air, most of the sample was colorless and transparent but some milky white pieces were also seen. It turned fully opaque and white and appeared sintered after heating at 1000 °C for 2 hr. A small concentration of alpha quartz (ref. 19) had precipitated out which is evident from the x-ray diffraction peaks (fig. 15); the M9S sample showed much stronger diffraction peaks of alpha quartz after similar heat treatment. The 2MS and 5MS samples were fired for 2 hr each at 1000, 1100, and 1200 °C and subjected to powder x-ray diffraction. The same crystalline phase, alpha quartz, was found to be present after each of the above thermal treatments. Gels containing 15 and 20 mol % MgO, after having been fired at 1000 °C for 2 hr, showed only a weak diffraction peak (fig. 15) at d = 3.754 Å (2θ = 23.7°) which could not be ascribed to any known phase comprising MgO and SiO_2.

Surface Area and Pore Size Distribution

BET surface area and pore volume were measured after densification of the gels at various temperatures. The pore volume and BET surface area calculated from the adsorption isotherms are presented in figure 16 for the $10MgO\text{-}90SiO_2$ (mol %) composition as a function of the firing temperature. Heat treatments at subsequent temperatures are cumulative; details are given in table VI. The pore volume initially increases to a maximum value at ~300 °C, then slowly decreases on further increase in temperature followed by a sharp decrease at ~890 °C. The surface area increases to a maximum value at ~500 °C and shows a sharp reduction at ~890 °C similar to the pore volume. The increase in surface area and pore volume at lower temperatures may be attributed to decomposition of nitrate and the loss of physically adsorbed water and residual organics trapped in the micropores of the dried gel. This is consistent with the results of DTA and TGA (vide supra). The reduction in surface area and pore volume at higher temperatures would probably correspond (ref. 30) to an increase in the degree of crosslinking as the decomposition of silanols leads to polymerization. The rapid decrease in both surface area and pore volume at ~890 °C represents an increase in density due to sintering.

DISCUSSION

The time taken to complete a process gives an estimate of rate of the reaction. Gelling time sharply decreased with increase in reaction temperature (table III) indicating a faster rate of hydrolysis and polymerization at higher temperatures. However, an increase in temperature causes an increase in rates of both hydrolysis and polymerization but the effect (ref. 31) is not the same for both these processes. Generally the influence of reaction temperature is smaller for polymerization than for hydrolysis because the former involves diffusion of partially hydrolyzed species while the latter is a more direct process. High temperature hydrolysis results in smaller particles with more highly structured networks. Temperature dependence of the overall (hydrolysis and condensation) reaction may be expressed by an Arrhenius type equation:

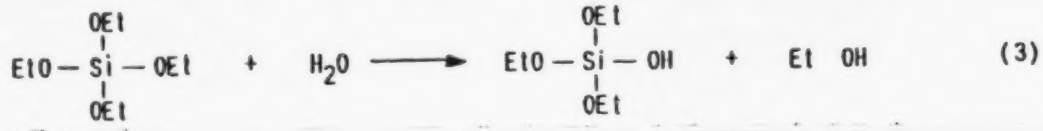
$$t = A \exp[E/RT] \qquad (1)$$

where t is the gelation time, A the preexponential term, E the activation energy for the overall gelation (hydrolysis and polymerization) process, R the gas constant, and T the reaction temperature in degrees K. Taking the logarithm of equation (1) gives

$$\log t = \log A + \frac{E}{(2.3026RT)} \qquad (2)$$

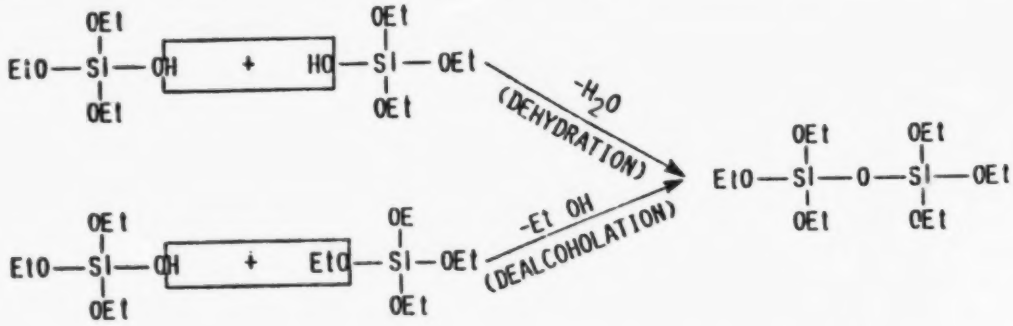
according to which a plot of log t against 1/T should be linear with slope E/2.3026R. The plot of log t versus 1/T for the $10MgO\text{-}90SiO_2$ system using a water:TEOS mole ratio of 7.5 is linear (fig. 17) indicating applicability of equation (1). From a linear least-squares fit the activation energy is calculated to be 58.7 kJ/mol ($A = 1.06 \times 10^{-19}$ with a correlation coefficient = 0.9998) for the gelling process in the temperature range 2 to 70 °C.

Gel formation proceeds through hydrolysis and condensation steps. When water is added to TEOS precursor solution, hydrolysis takes place:



(3)

where Et represents the ethyl group. The partially hydrolyzed species condenses with -OH or -OEt on other molecules resulting in



(4)

Si-O-Si bonds by dehydration or dealcoholation. This leads to the formation of oligomers in solution which upon further condensation results in the formation of a three-dimensional glass-like network. The system changes into a gel when polymerization is extensive. The water molecule regenerated during the condensation of -OH groups on two partially hydrolyzed species can be further utilized for hydrolysis of another -OEt group. Theoretically, only 2 mol of water/mol of TEOS are required for the complete hydrolysis and polymerization. In the present work clear and transparent homogeneous gels were obtained only when the water to TEOS mole ratio was greater than 4. When insufficient water (less than the stoichiometric amount needed for complete hydrolysis of TEOS) is added to the sol, gelation takes place by absorbing moisture from the ambient atmosphere. In such a case gelling of the solution starts from the surface and gradually develops into the bulk. By the time bulk gelation is complete, the gel surface has already started drying causing crystallization of magnesium nitrate hexahydrate from the supersaturated solution near the surface, resulting in white powder on gel surface. This problem could be

alleviated by initially adding a sufficient amount of water needed for complete hydrolysis of TEOS in the bulk solution as in the case of 10MS and M9S systems which resulted in clear, transparent, and homogeneous bulk gels.

The x-ray diffraction of dried gels containing up to 15 mol % magnesium oxide does not show the presence of any crystalline phase. This probably indicates that magnesium is not free and has been incorporated into the polymer (gel) network. However, it is not clear in what way the polymerizing TEOS has incorporated ions of the dissolved magnesium salt within the polymer (gel) network. Probably the Mg^{2+} ions are introduced into the gel network by a cation exchange reaction (ref. 32) between the metal cation and the weakly acidic silanol (≡Si-OH) group:

$$Mg^{2+} + 2(\equiv Si\text{-}OH) \rightleftharpoons Mg(OSi\equiv)_2 + 2H^+ \qquad (5)$$

Reaction 5 is reversible (ref. 32) in acidic solutions and is the sum of the following two reactions:

$$\equiv Si\text{-}OH \rightleftharpoons \equiv Si\text{-}O^- + H^+ \qquad (6)$$

and

$$Mg^{2+} + 2(\equiv Si\text{-}O^-) \rightleftharpoons Mg(OSi\equiv)_2 \qquad (7)$$

Gels containing higher concentrations of magnesium, 20MS, show the crystallization of magnesium nitrate hexahydrate on drying when the gel volume had reduced to about one-third of the original volume. This probably implies that only up to ~15 mol % magnesium can be incorporated into the polymer network in the form of magnesium nitrate using the sol-gel process. Crystallization of metal nitrate has also been reported by Yamane and Kojima (ref. 13) during the synthesis of $20SrO\text{-}80SiO_2$ (wt %) gels using strontium nitrate and silicon tetramethoxide as the starting materials. This phenomenon of crystallization of the metal salt from the gel during the drying step has been ascribed (ref. 13) to nonparticipation of the alkaline earth metal ions in either hydrolysis of silicon alkoxide or subsequent dehydration polymerization. The salt ions remain very mobile even after gelation because of the large liquid contents in the gel. At high concentrations of the alkaline earth metal ions, most of these ions remain in the liquid phase without being incorporated into the gel network. During the gel drying process, concentration of these ions in the liquid phase increases until supersaturation is reached and crystals start growing on the gel surface thereby destroying the homogeneity originally achieved by mixing in solutions. Mukherjee (ref. 17) has also observed crystallization of sodium nitrate on desiccating gels in the $Na_2O\text{-}B_2O_3\text{-}SiO_2$ system. In the study by Hayashi and Saito (ref. 11), hydrolysis of TEOS and calcium nitrate solutions resulted only in white powders probably due to the formation of calcium nitrate crystals from the gels on drying. In contrast, monolithic transparent $CaO\text{-}SiO_2$ glasses were obtained by hydrolysis of calcium ethoxide and TEOS with atmospheric moisture; hydrolysis by addition of water resulted in translucent or opaque bodies due to precipitation of calcium hydroxide.

SUMMARY AND CONCLUSIONS

Synthesis of $MgO-SiO_2$ glasses by the sol-gel process has been investigated as a function of various experimental parameters and the following conclusions may be drawn from the results of this study:

(1) $MgO-SiO_2$ glass compositions within the stable liquid-liquid immiscibility dome which cannot be prepared by the conventional glass melting method can be synthesized at low temperatures by the sol-gel technique.

(2) Introduction of a modifier cation in the form of a salt solution is not suitable for the synthesis of glasses with high modifier cation concentration. Only 15 mol % MgO can be incorporated into the silica network using magnesium nitrate. This is, however, significant as magnesium ethoxide has only limited solubility in alcohol.

(3) Gelling time decreased with increase in magnesium content, water:TEOS mole ratio, and reaction temperature.

(4) Clear, transparent, and homogeneous gels were obtained when water:TEOS mole ratio was 4 or more.

(5) Activation energy for gel formation in the $10MgO-90SiO_2$ (mol %) system at a water:TEOS mole ratio of 7.5 was found to be 58.7 kJ/mol.

(6) Alpha-quartz was the crystalline phase in the gels heated to ~950 °C.

(7) Trace amounts of -OH groups were detected by infrared spectroscopy even in specimens fired to ~890 °C. No absorption peaks attributable to organic groups were present.

(8) Monolithic dry gel bodies could be prepared using glycerol as the drying control chemical additive.

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TABLE IV. - EFFECT OF EXPERIMENTAL CONDITIONS ON GELLING TIME AND APPEARANCE FOR 10 MgO-90 SiO_2 (mol %) SYSTEM AT R. . TEMPERATURE

Acronym	$Si(OC_2H_5)_4$, g	$Mg(NO_3)_2 \cdot 6H_2O$ g	$Mg(CH_3COO)_2 \cdot 4H_2O$, g	C_2H_5OH, ml	Total water, g	$H_2O/Si(OC_2H_5)_4$, mole ratio	Gelling time, hr	Gel appearance
MS9A	45	6.164	----	80	2.6	0.67	312	Nonhomogeneous, white crystals on surface
MS9B					10.4	2.68	216	Nonhomogeneous, white crystals on surface
MS9C					15.6	4.00	90	Clear, transparent
10MS					22	5.66	33	Clear, transparent
M9S					32.8	8.44	22	Clear, transparent
10MAS		-- --	5.16		21.2	5.45	--	White powder

TABLE V. - INFRARED ABSORPTION PEAKS OBSERVED IN MgO-SiO_2 GELS AND GLASSES AND THEIR ASSIGNMENTS

Frequencies of IR absorption bands	Functional group
460 cm^{-1}	Bending modes of Si-O-Si bonds
800 cm^{-1}	Bending modes of O-Si-O bonds
~958 cm^{-1}	Si-OH bonds containing nonbridging oxygen
~1078 cm^{-1}	Stretching vibration of Si-O-Si bonds
1385 cm^{-1}	$-NO_3$ group
~1640 cm^{-1}	H_2O
~3450 cm^{-1}	H_2O

TABLE VI. - VALUES OF BET SURFACE AREA AND CUMULATIVE PORE VOLUME OF 10MgO-90SiO_2 (mol %) GEL AFTER VARIOUS THERMAL TREATMENTS

[Water: TEOS mole ratio = 5.66.]

Thermal treatment	BET surface area, m^2/g	Pore volume, cm^3/g
Gel dried at 72 °C for more than 6 days	371	0.151
As above + at 300 °C for 20 hr	672	0.301
As above + at 499 °C for 23 hr	690	0.246
As above + at 700 °C for 22.5 hr	625	0.204
As above + at 793 °C for 8.5 hr	530	0.177
As above + at 890 °C for 7.5 hr	54	0.004

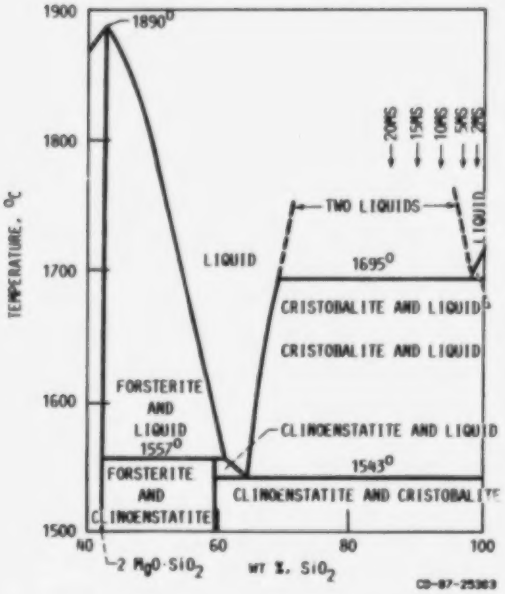

FIG. 1. - PARTIAL PHASE DIAGRAM OF MgO-SiO_2 SYSTEM SHOWING POSITIONS OF THE VARIOUS COMPOSITIONS STUDIED.

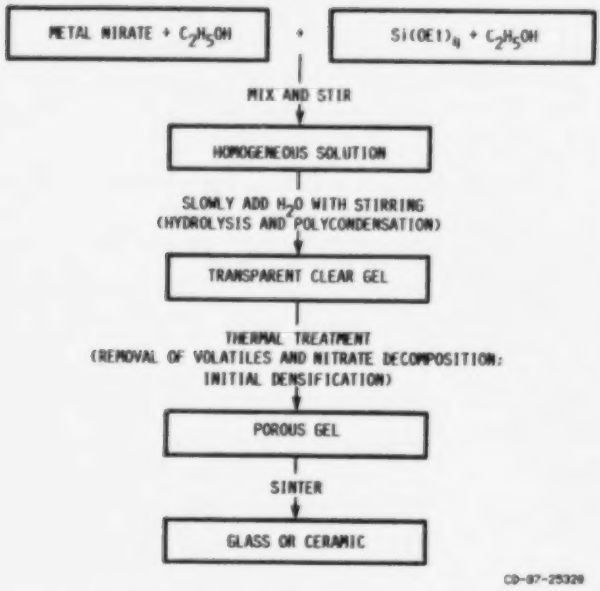

FIG. 2 - FLOW DIAGRAM OF THE SOL-GEL PROCESS FOR GLASS SYNTHESIS.

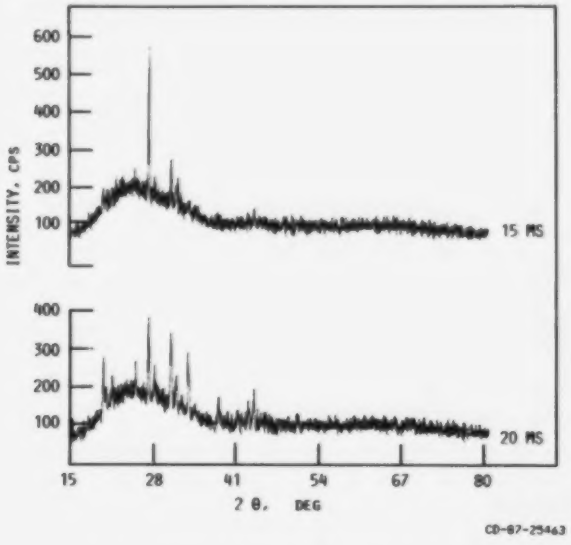

FIG. 3. - POWDER X-RAY DIFFRACTOGRAMS OF 15 MS AND 20 MS GELS DRIED AT ROOM TEMPERATURE. THE PEAKS CORRESPOND TO $Mg(NO_3)_2 \cdot 6H_2O$ CRYSTALS.

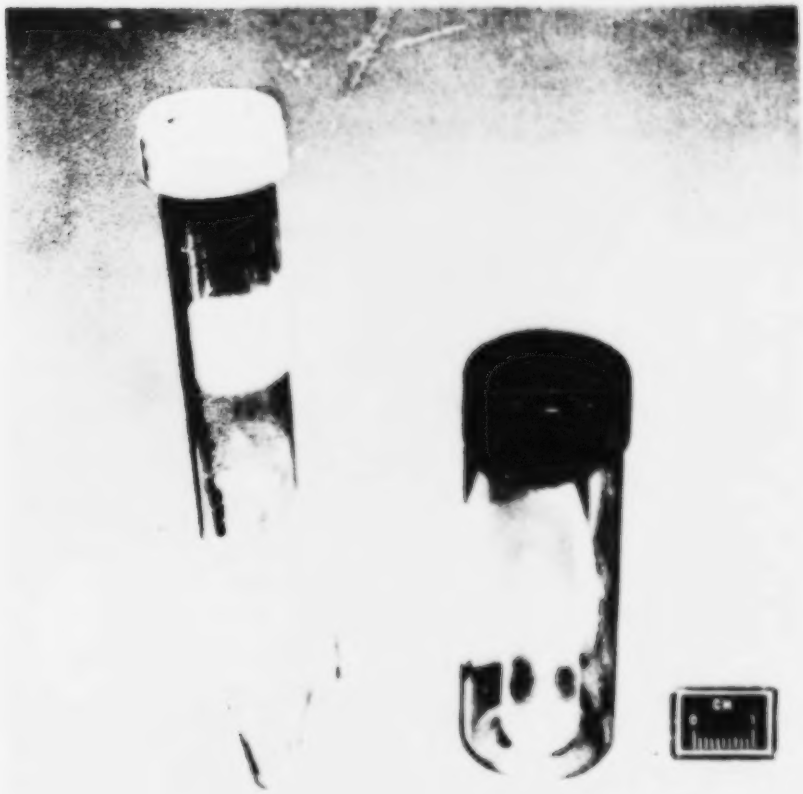

FIG. 4. - MONOLITHIC CYLINDRICAL SAMPLES OF $10MgO\text{-}90SiO_2$ (MOL %) COMPOSITION PREPARED USING GLYCEROL AS THE DRYING CONTROL CHEMICAL ADDITIVE (DCCA).

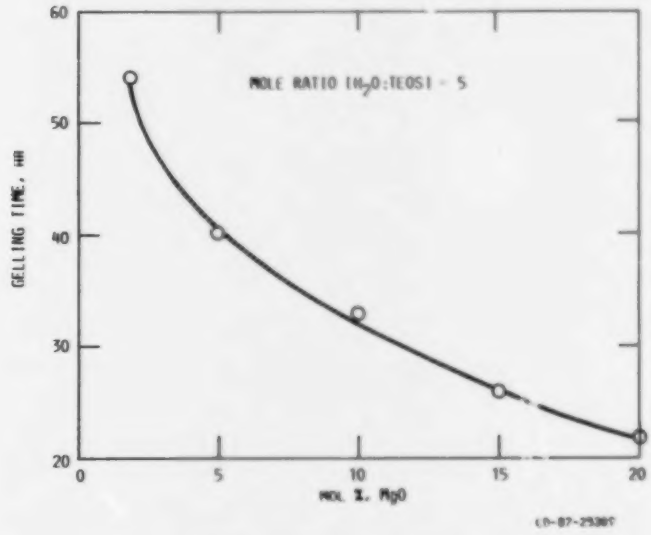

FIG. 5. - EFFECT OF MAGNESIUM OXIDE CONTENT ON TIME OF GEL FORMATION AT ROOM TEMPERATURE FOR THE $MgO\text{-}SiO_2$ SYSTEM: WATER:TEOS MOLE RATIO ~5.

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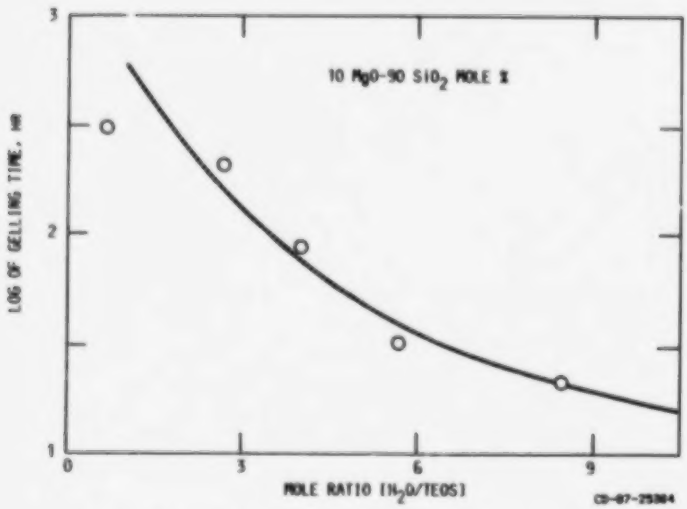

FIG. 6 - INFLUENCE OF WATER:TEOS MOLE RATIO ON TIME OF GELATION OF $10MgO\text{-}90SiO_2$ (MOL %) COMPOSITION AT ROOM TEMPERATURE.

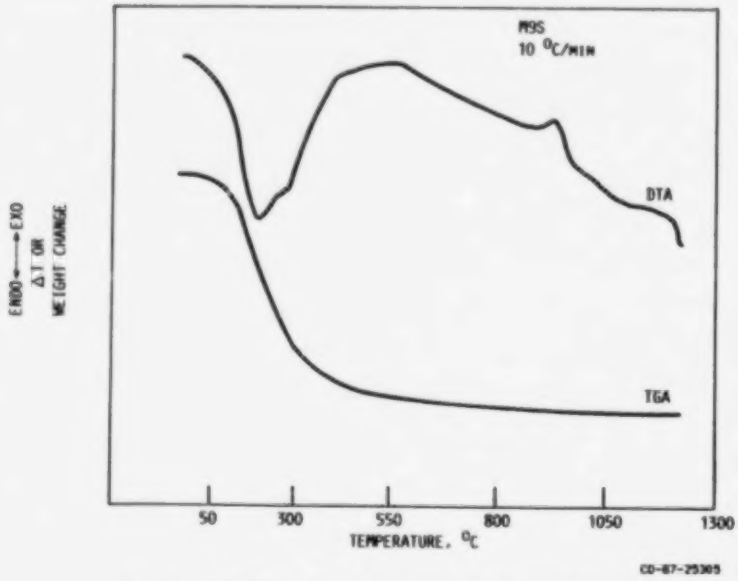

FIG. 7. - DTA AND TGA CURVES SIMULTANEOUSLY RECORDED ON THE SAME GEL SAMPLE OF COMPOSITION $10MgO\text{-}90SiO_2$ (MOL %) DRIED AT 76 °C FOR 50 HR: HEATING RATE 10 °C/MIN IN FLOWING AIR.

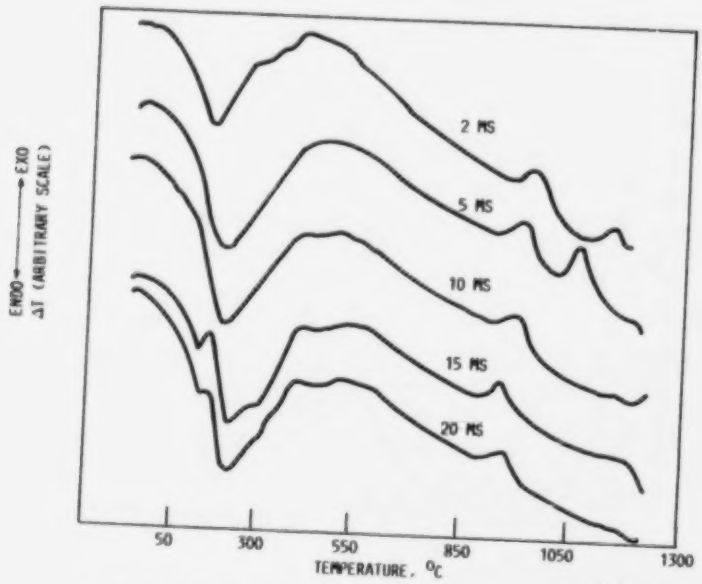

FIG. 8. - DTA CURVES OF $MgO\text{-}SiO_2$ GELS OF VARIOUS COMPOSITIONS DRIED AT 76 °C FOR 50 HR; SCAN RATE OF 10 °C/MIN IN FLOWING AIR.

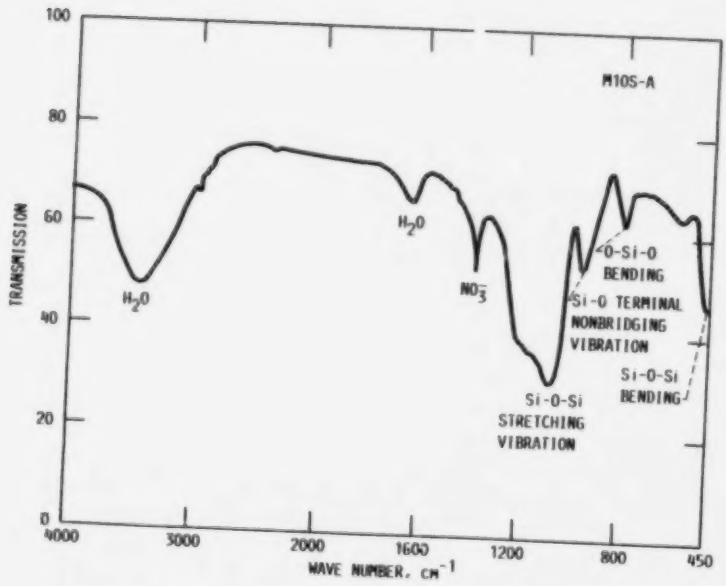

FIG. 9 - INFRARED SPECTRA OF $10MgO\text{-}90SiO_2$ (MOL%) GEL DRIED AT 72 °C FOR MORE THAN 6 DAYS; MOLE RATIO OF WATER:TEOS = 5.6.

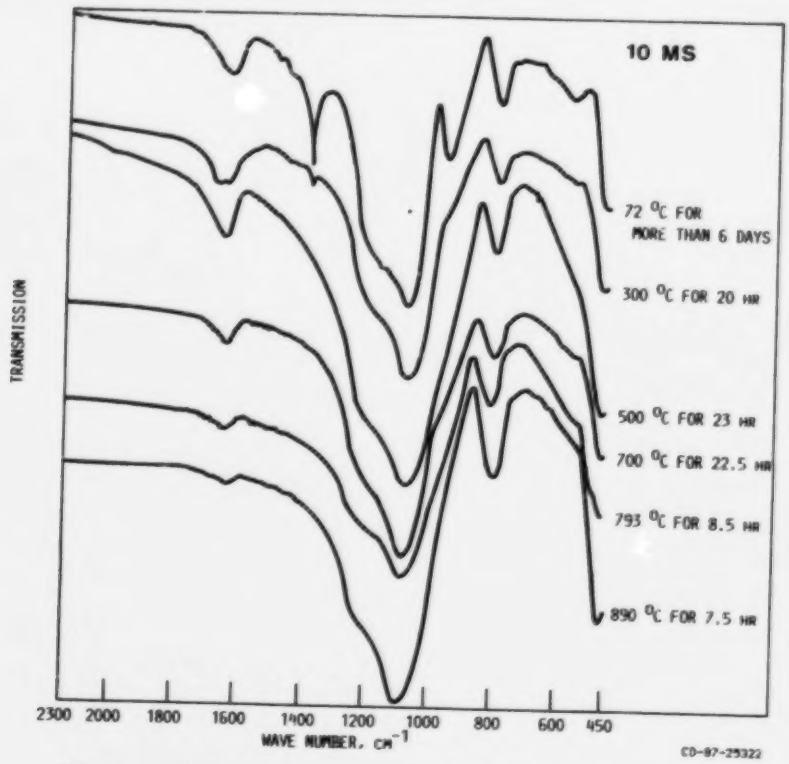

FIG. 10. - INFRARED SPECTRA OF $10MgO\text{-}90SiO_2$ (MOL %) GEL AFTER FIRING AT VARIOUS TEMPERATURES. THE HEAT TREATMENTS ARE CUMULATIVE AT SUBSEQUENT TEMPERATURES.

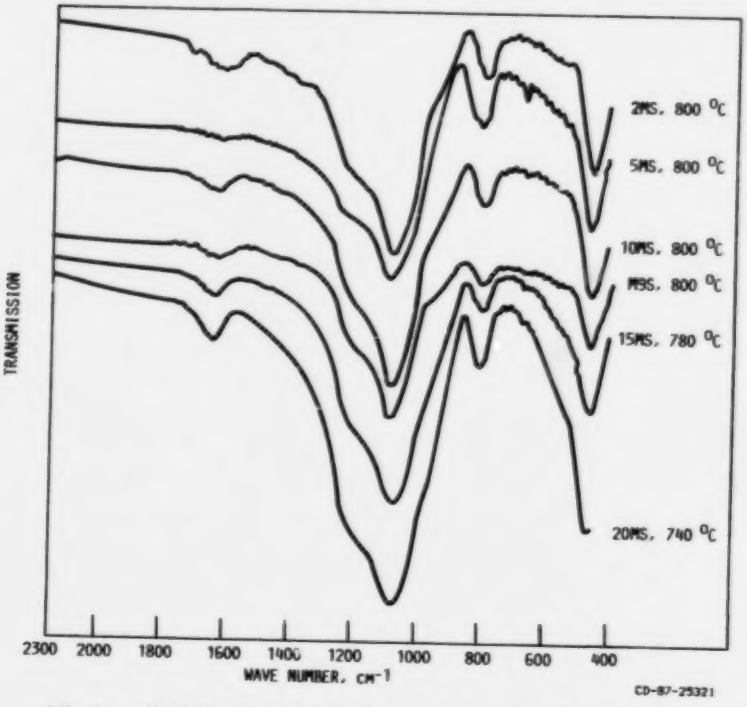

FIG. 11. - INFRARED SPECTRA OF $MgO\text{-}SiO_2$ GELS OF DIFFERENT COMPOSITIONS AFTER BEING FIRED TO VARIOUS TEMPERATURES AT 3 °C/MIN IN FLOWING AIR AND FURNACE COOLED.

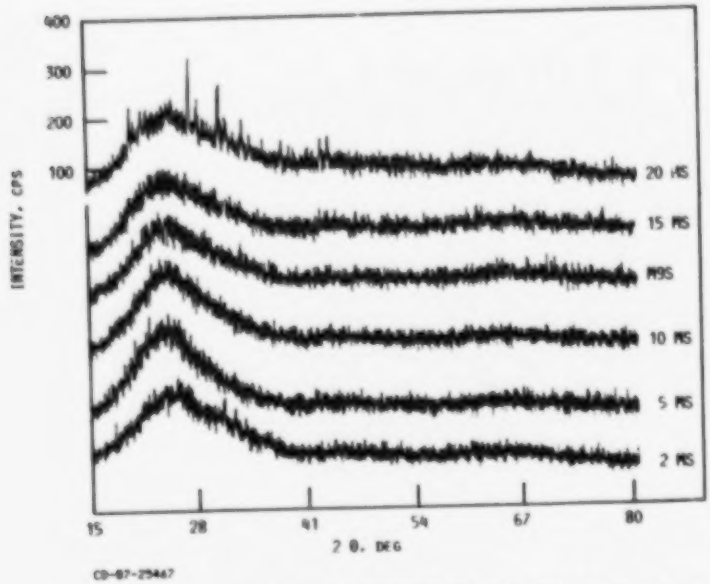

FIG. 12. - X-RAY DIFFRACTION PATTERNS OF $MgO\text{-}SiO_2$ GELS OF VARIOUS COMPOSITIONS DRIED AT 76 °C. THE PEAKS IN 20 MS SAMPLE CORRESPOND TO $Mg(NO_3)_2 \cdot 6H_2O$ CRYSTALS.

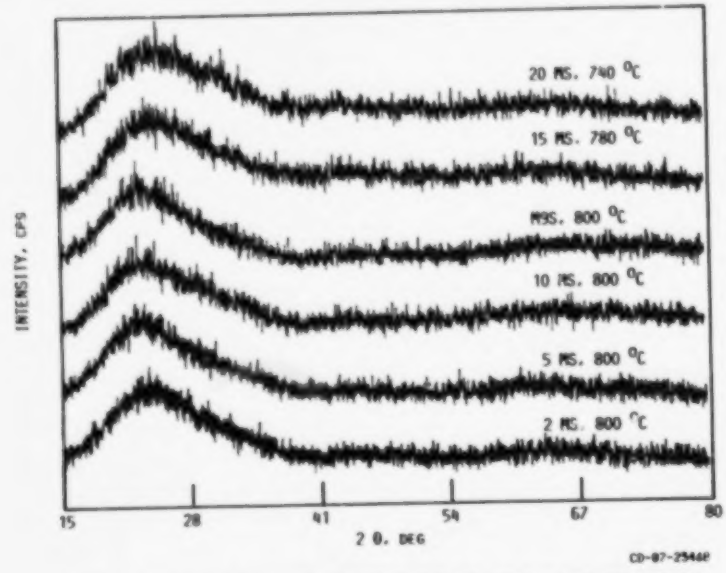

FIG. 13. - X-RAY DIFFRACTION SPECTRA OF $MgO\text{-}SiO_2$ GELS OF VARIOUS COMPOSITIONS HEATED TO DIFFERENT TEMPERATURES IN FLOWING AIR AT 3 °C/MIN AND FURNACE COOLED.

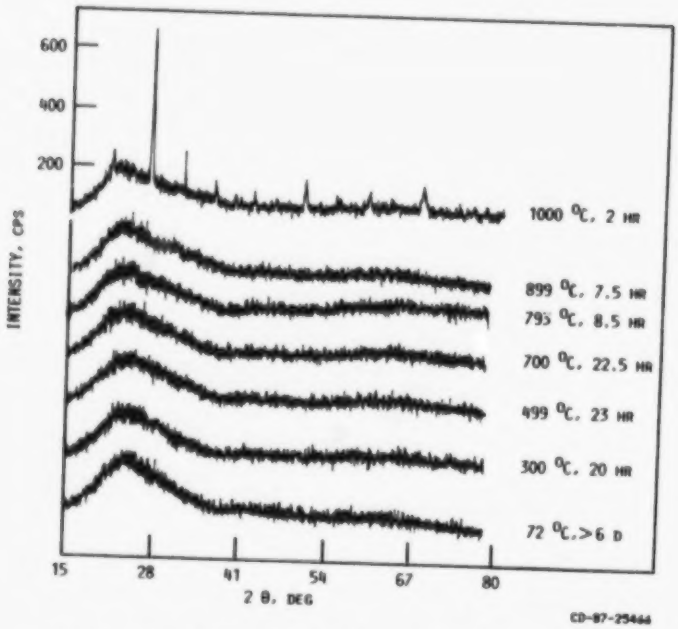

FIG. 14. - X-RAY DIFFRACTOGRAMS OF 10 MgO-90SiO_2(MOL%) COMPOSITION GEL FIRED AT DIFFERENT TEMPERATURES FOR VARIOUS LENGTHS OF TIME; PEAKS IN THE 1000 °C FIRED SAMPLE CORRESPOND TO α-QUARTZ CRYSTALS.

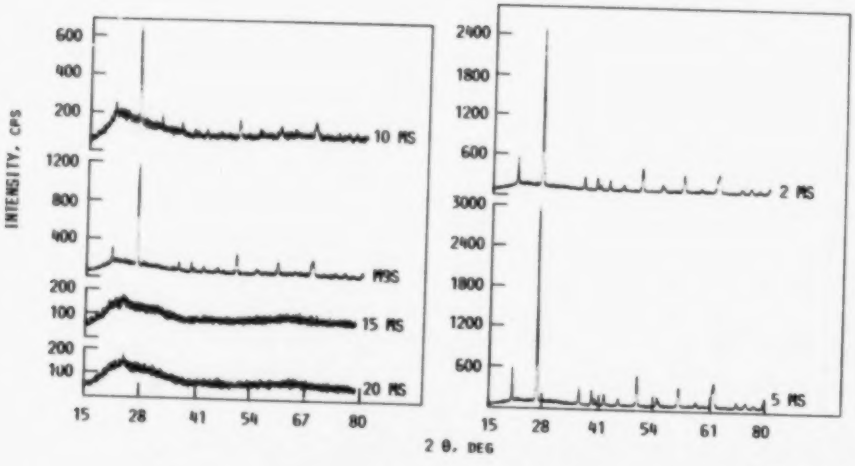

FIG. 15. - POWDER X-RAY DIFFRACTION SCANS OF MgO-SiO_2 GELS OF VARIOUS COMPOSITIONS FIRED AT 1000 °C FOR 2 HR; SHARP DIFFRACTION PEAKS IN 2 MS, 5 MS, 10 MS, AND M9S SAMPLES CORRESPOND TO α-QUARTZ CRYSTALS.

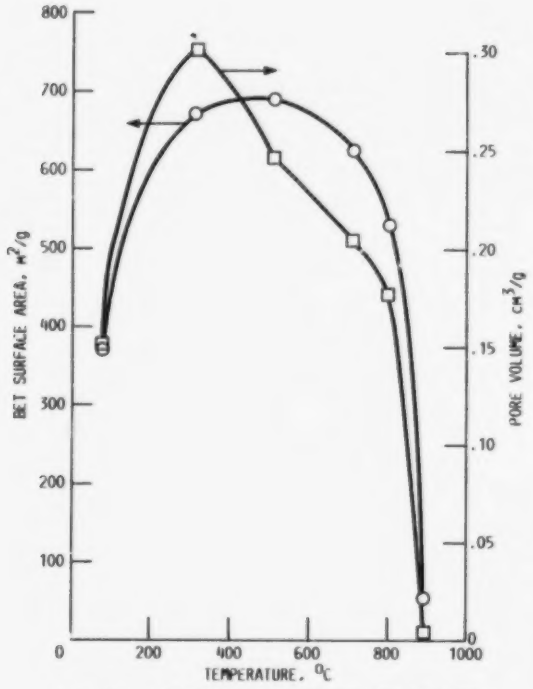

FIG. 16. - VARIATION OF BET SURFACE AREA AND PORE VOLUME WITH FIRING TEMPERATURE OF $10MgO\text{-}90SiO_2$ (MOL %) GEL COMPOSITION; WATER: TEOS MOLE RATIO = 5.66. THE THERMAL TREATMENTS ARE CUMULATIVE AT SUBSEQUENT TEMPERATURES (SEE TABLE VI FOR DETAILS).

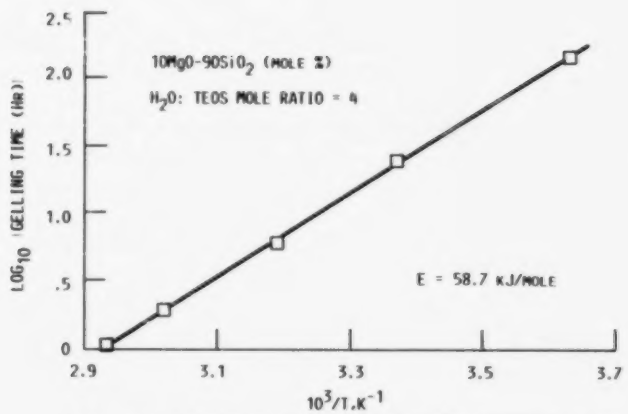

FIG. 17. - ARRHENIUS PLOT SHOWING TEMPERATURE DEPENDENCE OF GELLING TIME OF $10MgO\text{-}90SiO_2$ (MOL %) COMPOSITION; WATER:TEOS MOLE RATIO = 7.5.

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15. Supplementary Notes
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16. Abstract
$MgO-SiO_2$ glasses containing upto 15 mol % MgO, which could not have been prepared by the conventional glass melting method due to the presence of stable liquid-liquid immiscibility, have been synthesized by the sol-gel technique. Clear and transparent gels were obtained from the hydrolysis and polycondensation of silicon tetraethoxide (TEOS) and magnesium nitrate hexahydrate when the water: TEOS mole ratio was four or more. The gelling time decreased with increase in magnesium content, water: TEOS ratio, and reaction temperature. Magnesium nitrate hexahydrate crystallized out of the gels containing 15 and 20 mol % MgO on slow drying. This problem was partially alleviated by drying the gels quickly at higher temperatures. Monolithic gel samples were prepared using glycerol as the drying control chemical additive. The gels were subjected to various thermal treatments and characterized using techniques such as DTA, TGA, IR-spectroscopy, x-ray diffraction, surface area and pore size distribution measurements. No organic groups could be detected in the glasses after heat treatments to ~800 °C, but trace amounts of hydroxyl groups were still present. No crystalline phase was found from x-ray diffraction in the gel samples heated to ~890 °C. At higher temperatures, alpha quartz precipitated out as the crystalline phase in gels containing up to 10 mol % MgO. The weak diffraction peaks in heated samples containing 15 and 20 mol % MgO could not be assigned to any known phase. The overall activation energy for gel formation in $10MgO-90SiO_2$ (mol %) system for water: TEOS mole ratio of four was calculated to be 67 kJ/mol.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Sol-Gel; Glasses; Liquid-Liquid immiscibility; Infrared spectroscopy; X-ray diffraction; DTA; TGA	Unclassified - unlimited STAR Category 27

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